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**ALUMINUM-NITROGEN AND
ALUMINUM-PHOSPHORUS POLYMERS**

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FOREWORD

The research reported in this document was conducted by Drs. A. R. Cullingworth, K. Gosling, J. D. Smith, and D. Wharmby, Chemical Laboratory, University of Sussex, Falmer, Brighton, Sussex, England. The work was performed under Grants No. EOAR 64-77 and No. EOAR 65-88 administered through the European Office of Aerospace Research, United States Air Force. The grants were initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena," Task No. 734201, "Basic Factors in the Synthesis of Macromolecular Materials." The work was sponsored by the Air Force Materials Laboratory, Directorate of Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. Harold Rosenberg as Project Engineer.

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This report has been reviewed and is approved.



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ABSTRACT

The products of the reaction between methylamine and trialkylaluminiums have been studied by molecular weight determinations as well as by infrared and nuclear magnetic resonance spectroscopy. Stereoisomers of $(R_2AlNHR)_3$ are indicated. The reactions of phosphine adducts of organoaluminium compounds have been studied and an order of base strength with respect to triethylaluminium has been established by displacement reactions. Polymers of composition $(RAlPR')_x$ have been prepared but crystalline products have not been obtained. Aluminium-nitrogen seem to be more stable than corresponding aluminium-phosphorus frameworks.

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TABLE OF CONTENTS

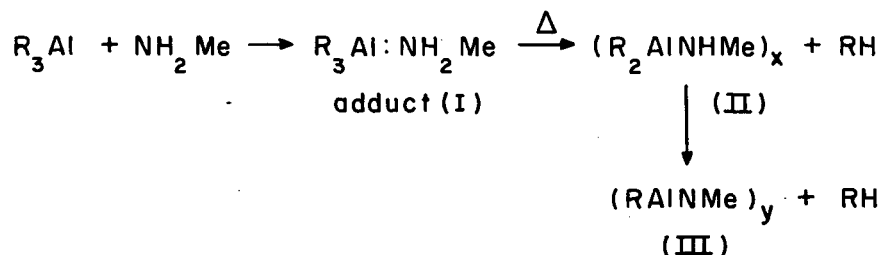
SECTION	PAGE
I ALUMINIUM-NITROGEN POLYMERS	1
1. Introduction	1
2. Reactions Between Trimethylaluminium and Methylamine	2
3. Reactions Between Triethylaluminium and Methylamine	6
4. Possible Dehydrohalogenation Reactions	9
5. Ammonia Adducts of Phenylaluminium Compounds	11
II ALUMINIUM-PHOSPHORUS POLYMERS	13
1. Introduction	13
2. Reactions of Donor-Acceptor Complexes	14
3. Preparation and Reactions of Diethyl(dimethylphosphinyl)aluminium	15
4. Preparation of the Compounds $(RPAIR)_x$	16
5. NMR Data on Adducts of Phosphorus Esters With Organoaluminium Compounds	17
REFERENCES	21

SECTION I

ALUMINIUM-NITROGEN POLYMERS

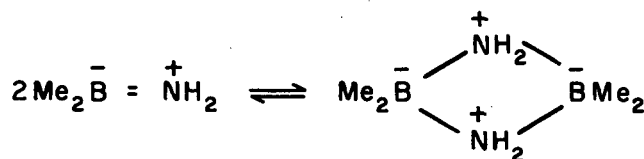
1. INTRODUCTION

Although it has been known for some time that the thermal decomposition of the monomeric adducts formed between aluminium trialkyls and methylamine leads to the evolution of an alkane and formation of Al-N polymers in two distinct stages (References 1 and 2), the elucidation of the structures of the polymeric materials has received little attention.



Compounds of type II have been isolated and shown (Reference 3) to be low polymers in benzene solution, but no detailed structural data (e.g., crystal structures or detailed analyses of spectra) have been published. Of the compounds of type III, only the compound (PhAlNPh) has been studied in detail from a structural point of view. The latter substance was shown to have a tetrameric cubane structure in the crystal. Other materials, e.g., ClAlNMe, are usually obtained in the amorphous state, but crystalline tetrameric forms can be isolated by careful control of reaction conditions (Reference 4). These tetramers are not suitable for spectral or other structural studies because of their low volatility and low solubility in organic solvents. They are thus difficult to purify.

Many of the corresponding boron compounds of type II, R_2BNHMe , are monomeric and this has been attributed to π delocalisation, e.g., $N \rightleftharpoons B$ (Reference 5). If, however, alkyl groups attached to boron or nitrogen are replaced by more electronegative atoms, dimeric species may result. In some cases an equilibrium between monomer and dimer may be detected, e.g.,



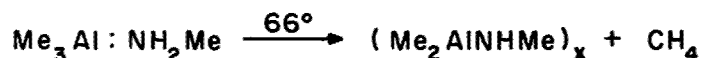
Boron compounds of type III are usually trimeric (borazines), but cyclic tetramers, e.g. $(t\text{-BuNBCl})_4$, are obtained from highly hindered amines (Reference 6).

In the present investigation the compounds $(R_2AlNHMe)_x$ and $(RAINMe)_y$ (where $R = Me, Et$) have been reexamined, since these are volatile and soluble in organic solvents. It was hoped that the Al-Me compounds would have structures that were sufficiently simple for a complete analysis of their spectra to be achieved. The $Me_3Al:NH_2Me$ system was first

studied by Wiberg and reported by Bähr (Reference 1). The intermediate (I, R = Me) melted between 55° and 57° with evolution of methane and formation of a crystalline compound (II, R = Me) which, in turn, melted at 110° with the expulsion of more methane and the formation of a glassy, nonvolatile high polymer (III, R = Me). No molecular weight data was published.

2. REACTIONS BETWEEN TRIMETHYALUMINIUM AND METHYLAMINE

The objectives of the initial experiments were to check the stoichiometry of the pyrolyses carried out by Wiberg (Reference 1) and to measure the methane evolved. It was found to be impossible to carry out the reaction in a solvent (hexane, toluene or Tetralin) under vacuum because the initial adduct sublimed out of the reaction mixture and complete decomposition could not be achieved. However, the decomposition was successfully carried out in the absence of solvent in a large sealed bulb at 66° and the methane evolved was found to correspond to 1.005 moles/mole of adduct for the equation:



The solid residue was initially soluble in hexane, but after filtering through a sintered disc under nitrogen, it precipitated again as fine needles. These could be recrystallised under nitrogen from hexane/toluene (10%) or sublimed at 50° under high vacuum to give a compound with a mp of 108° to 110° which was sufficiently sharp to suggest reasonable purity.

Hydrolysis with dilute sulfuric acid gave the following results in moles/mole of $(\text{Me}_2\text{AlNHMe})$:

MeH		Al (as 8-hydroxyquinolate)		MeNH ₂ (by Kjeldahl)	
Obs	Calc	Obs	Calc	Obs	Calc
2.03	2.00	1.04	1.00	0.998	1.00

These results indicated that the basic unit of the system is indeed $(\text{Me}_2\text{AlNHMe})$.

Cryoscopic molecular weight determination in benzene solution gave a value of 267 which, within experimental error, agrees with the value of 261 calculated for the trimer $(\text{Me}_2\text{AlNHMe})_3$. The mass spectrum showed a very weak peak at 261 mc for the trimer parent ion, but a much stronger peak at 246 mc which would correspond to the loss of a methyl group from the trimer.

The infrared spectra of Nujol and hexachlorobutadiene mulls obtained on a Perkin-Elmer Model 337 Spectrometer is shown in Table I.

TABLE I
INFRARED SPECTRUM OF $(\text{Me}_2\text{AlNHMe})_3$

cm ⁻¹	Tentative Assignment
3240 s	N-H ν
2980 m	C-H ν
2970 m	
2930 s	
2890 m	
2815 m	

TABLE I (continued)

cm ⁻¹	Tentative Assignment
1470 w } 1465 w }	$\delta_{as} (\text{CH}_3)$
1335 w	
1260 w	
1190 b-s	
1140 m	
1070 w	
1045 m	
1068 b-s	
680 b-s	
615 b-s	
640 m	

NOTE: as = asymmetric; b = broad; m = medium; s = strong; w = weak.

The significant region of the spectrum shows only one N-H stretching vibration at 3240 cm⁻¹ indicating that all the N-H bonds are equivalent or so close in energy as to preclude their resolution. This would be in agreement with a cyclic rather than a linear trimer.

An X-ray powder pattern of the solid showed that the polymer was crystalline.

The proton magnetic resonance (PMR) spectrum in benzene solution at room temperature shows the following peaks in which the values refer to chemical shifts from T.M.S. at 10.00 ppm:

N-CH ₃	Al-CH ₃	^J H-N-C-H
τ 8.04 ppm	10.68 ppm	6.7 cps and 6.6 cps

The N-Me region of the spectrum showed two doublets. This seems to indicate that there are two different methyl groups present in solution (and hence two different nitrogen protons which is not in agreement with the IR data on solid mulls) and that the signal from the protons of each methyl group is split by a proton on nitrogen. Unfortunately it is not possible to identify the nitrogen proton resonances (which should be two quartets through interaction with the different methyl groups) because they are weak due to quadrupole broadening and also because they are probably masked by the Al-Me resonances. The three peaks in the Al-Me region cannot otherwise be readily explained.

Although the N-Me proton resonances are split into a pair of doublets, there is no simple relationship between the areas under the peaks, as there should be for a cyclohexane-type cyclic trimer, with two of one sort of methyl group, and one of another, e.g.,



From this experiment, there was no evidence for the formation of more than one compound, although it was apparent that some sudden change had occurred when the compound was dissolved in hexane.

In another experiment, the crude reaction mixture was separated by trap-to-trap fractional condensation under high vacuum. This gave three main fractions:

- a. A liquid (mp ca 0°), vapour pressure ca 1.5 mm at 18° which passed through a -6° trap, but was stopped in one at -15°. This compound deposited a solid residue (which proved to be b) each time it was distilled and therefore could not be obtained in a pure state. The mass spectrum was completely different than that obtained for fractions b and c, and could not be readily understood.
- b. A solid (mp 115°-117°), just volatile enough to be distilled in the vacuum line at room temperature, and which was stopped in a 10° trap.
- c. A solid, involatile at room temperature, but which could be sublimed at 50° under high vacuum. This compound proved to be identical with the recrystallised product from the previous experiment (X-ray powder pattern, IR spectrum, mass spectrum, and nuclear magnetic resonance (NMR) spectrum, mp)

So far, the physical difference between fractions b and c has been difficult to understand. IR, NMR, and mass spectra are identical but volatility, mp, and X-ray powder patterns (Table II) are different. It is tentatively supposed that, in solution, fractions b and c are in equilibrium and that it is fraction c which is the most stable crystalline form which separates from solution. If this is so, then low-temperature NMR should indicate such an equilibrium and, when this is available, it should be possible to elucidate this problem so as to determine the structure of b and c.

TABLE II
X-RAY POWDER DATA FOR $(\text{Me}_2\text{AlNHMe})_3$

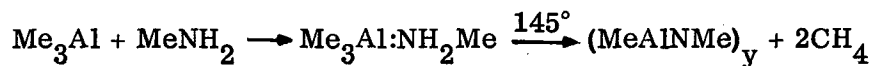
b. Rhombs (Sublimes at 20°)		c. Needles (Sublimes at 50°)	
d.	Intensity	d.	Intensity
7.91	vs	7.99	vs
7.58	ms	5.58	vs
5.90	vs	4.76	vw
5.71	m	4.67	m-w
5.53	ms	3.59	m-s
4.64	m	3.60	w
3.93	m	3.29	vw
3.80	m	3.22	vw
3.65	w	3.03	m-w
3.26	m	2.96	m-s
3.13	m	2.78	w
2.97	m	2.63	w
2.79	m	2.53	vw
2.64	w	2.39	m-w
2.54	m	2.27	vw
2.48	w	2.19	m-w
2.40	w	2.11	vw

TABLE II (Continued)

b. Rhombs (Sublimes at 20°)		c. Needles (Sublimes at 50°)	
d.	Intensity	d.	Intensity
2.33	w	2.05	vvw
2.26	w	2.02	w
2.09	w	1.96	m
2.01	w	1.92	m-w
1.96	vw	1.81	m-w
1.93	vw	1.77	w
1.72	w	1.73	vw
1.67	w	1.68	vvw
		1.65	vw
		1.61	vvw
		1.58	vvw
		1.55	vvw
		1.52	vw
		1.49	vw
		1.46	vvw
		1.44	vvw
		1.42	vw
		1.40	vvw
		1.37	vvw
		1.35	vvw
		1.34	vvw
		1.32	vw
		1.30	vvw
		1.28	vvw
		1.27	vvw
		1.23	vvw
		1.20	vw
		1.18	vvw
		1.16	vvw
7.91	vs	7.99	vs

NOTE: m = medium; s = strong; v = very; w = weak

In another series of experiments the adduct, $\text{Me}_3\text{Al:NH}_2\text{Me}$, was dissolved in Tetralin and heated to 145° for 15 hours in a large sealed bulb. The methane evolved corresponded to 1.92 moles/mole of adduct to confirm the equation:



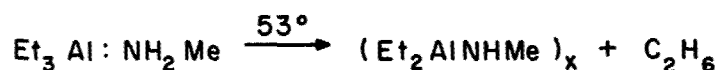
The residue was crystalline and soluble in benzene, but less so in hexane. It is promising that soluble, crystalline products have been obtained which point to low polymers and pure compounds.

3. REACTIONS BETWEEN TRIETHYLALUMINIUM AND METHYLAMINE

A mixture of equimolar quantities of triethylaluminium and methylamine in hexane was heated to 53° for 14 hours. After careful removal of solvent at -20°, a colourless liquid remained. Hydrolysis of a sample with dilute sulfuric acid led to the following analysis:

EtH		Al (as 8-hydroxyquinolate)		MeNH ₂ (by Kjeldahl)	
Obs	Calc	Obs	Calc	Obs	Calc
1.98	2.00	0.984	1.00	0.96	1.00

This data indicated that the reaction, as in the case of the methyl compound, has gone according to the equation:



The infrared spectrum showed two distinct peaks of equal intensity at 3315 and 3270 cm⁻¹ attributable to N-H stretching vibrations. The NMR spectrum of the neat liquid showed a pair of almost equally intense doublets partially superimposed upon each other in the region of the spectrum where nitrogen-methyl group protons should be found. This spectroscopic evidence indicated that the compound was not a single substance, although the analysis showed that (Et₂AlNHMe) was the basic unit involved. A dimer of this unit could have two possible isomers:



A cyclic trimer with a six-membered nonplanar Al-N ring system in the preferred cyclohexane chair configuration could have two sterically favoured isomers:

- With all nitrogen-methyl groups equatorial to the ring;
- With two nitrogen-methyl groups equatorial and one axial to the ring.

Distillation of the initial reaction product in an all-glass still under high vacuum gave two fractions:

(a) bp 35°-37°

(b) bp 115°

The mass spectrum of (b) showed a strong peak at 316 mc due to loss of an ethyl group. This is evidence for the trimeric form, but must be confirmed by molecular weight determination.

The IR spectra of the two fractions (Table II) differ most markedly in the N-H stretching region where the two peaks in the initial product are still present, but the intensity has changed remarkably. Fraction (a) has a medium peak at 3315 cm⁻¹ and a very weak absorption at 3268 cm⁻¹ while fraction (b) has the reverse.

TABLE III
INFRARED SPECTRA OF Et_2AlNHMe

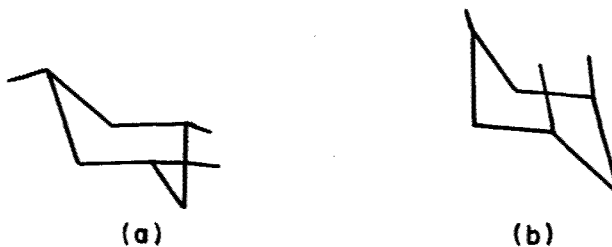
Fraction a (bp 35 -37) cm^{-1}	Fraction b (bp 115) cm^{-1}
3310 m	3313 vw
3270 w	3268 m
2988 inf-ms	2988 inf-ms
2938 vs	2938 vs
2905 vs	2904 vs
2868 vs	2867 vs
2830 m	
2795 m	2798 m
2730 mw	2732 w
1480 ms	
1470 ms	1468 ms
1412 ms	1410 ms
1378 m	1378 w
1355 ms	
	1330 ms
1230 m	1232 m
1195 ms	1197 ms
1167 w	
1139 m	1143 m
1108 m	1108 w
1063 s	1065 sh-m
	1045 ms
1026 vs	1027 sh-ms
983 vs	
	975 vs
952 s	953 s
	937 s
920 m	
906 inf-ms	905 s
875 m	

TABLE III (Continued)

Fraction a (bp 35°-37°) cm ⁻¹	Fraction b (bp 115°) cm ⁻¹
844 s	
807 s	833 m
660 vs	807 m
630 vs	654 vs
558 s	627 vs
512 m	
479 m	
	470 b-w

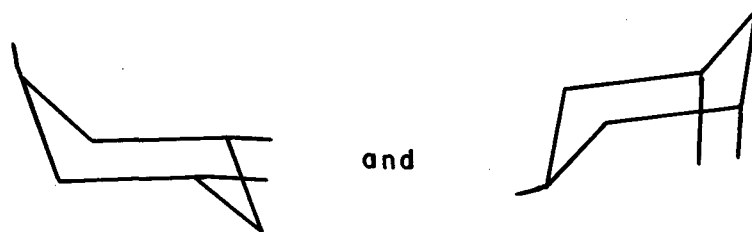
NOTE: b = broad; inf = inflection; m = medium; v = very;
s = strong; sh = shoulder; w = weak.

The NMR spectra of the two fractions also differ. The spectrum of each fraction shows only one doublet, and these correspond to the doublets in the spectrum of the mixture. The doublet from fraction (a) is clean both from the neat liquid and from benzene solution. This suggests that all the methyl groups are equivalent as in (a)



where all the methyl groups are equatorial. The methyl groups are still equivalent in the inverted (all axial) from (b), so that even if the energy barrier to inversion is low and inversion fast compared with the difference in chemical shifts of the axial and equatorial methyl groups, only one doublet would be observed in the spectrum. It may be possible to slow inversions by

cooling so that the low-temperature spectrum would be interesting. The spectrum of fraction (b) shows a clean doublet in the N-Me region in the neat liquid, but the doublet is further split (with no simple ratio of peak areas) in benzene solution. This may indicate an equilibrium between the forms



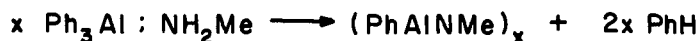
Again, spectra at various temperatures should confirm this suggestion.

This work at present looks promising. It should be possible to elucidate the structures of the various fractions and to measure their relative proportions. The importance of these results is twofold. First, comparison of data for methylamine and *t*-butylamine derivatives should throw light on the still unsolved problem of what determines ring size in Al-N polymers, and in particular should give information about steric factors. Secondly, if the isomers



are confirmed, it should be possible to examine whether they can be interconverted. This would involve breaking and making of Al-N bonds, and would give important data on the stability of cyclic Al-N ring polymers.

The adduct, $\text{Et}_3\text{Al}:\text{NH}_2\text{Me}$, dissolved in Tetralin, was heated to 190° for five hours in a nitrogen atmosphere. The solvent was removed under vacuum to give a white crystalline product, soluble in hexane. This suggests a low polymer which, if a single compound, should be capable of full characterisation. Similarly, when the adduct, $\text{Ph}_3\text{Al}:\text{NH}_2\text{Me}$, was refluxed in Tetralin for 25 hours, benzene (1.96 moles/mole of triphenylaluminium) was eliminated as estimated by vapour phase chromatography. This indicates that the following reaction occurred:



The yellow solid obtained by removal of solvent from the clear Tetralin solution was soluble in aromatic solvents and was recrystallised with difficulty from pentane/benzene. (Found: C, 66.5; H, 6.5; N, 9.6; Al, 18.6. Calc for PhAlNMe : C, 63.2; H, 6.1; N, 10.5; Al 20.3%). The discrepancy in the analysis may be due to the solvent of crystallisation. This material was previously obtained (Reference 7) in amorphous form; molecular weight and mass spectral measurements on the soluble form described here are being made.

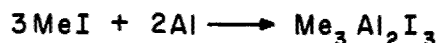
4. POSSIBLE DEHYDROHALOGENATION REACTIONS

So far dehydrohalogenation reactions have not been found to take place in Al-N systems. In compounds such as $(\text{MeH}_2\text{N}:\text{AlEtCl}_2)$ pyrolysis at 125° gave one mole of ethane and the

resulting polymeric compound $(\text{MeHNAI}\text{Cl}_2)_x$ was stable to 250° . In neither case was the evolution of hydrogen chloride or alkyl chloride observed (Reference 2). Jones and McDonald (Reference 3) (reporting the unpublished work of Jones and Hughes) go so far as to say that it is not possible to eliminate hydrogen halide, thermally or chemically, when there is a hydrogen on nitrogen and a halogen on aluminium, and cite the very high stability of $\text{H}_3\text{NAI}\text{Cl}_3$ as an example.

There is no evidence, however, that dehydrohalogenation has been attempted using compounds with iodine attached to aluminium. It is possible that $(\text{MeNH}_2:\text{AlMe}_2\text{I})$ could be induced to undergo chemical dehydrohalogenation rather than pyrolytic loss of methane if the hydrogen iodide could be removed by a low temperature reaction with base. The base must be strong enough to accept hydrogen iodide strongly but not strong enough to displace methylamine from the initial adduct. Triethylamine should be suitable.

With this idea in mind, the preparation of dimethylaluminium iodide and methylaluminium diiodide has been undertaken through the reaction of methyl iodide with activated aluminium wire (Reference 8).



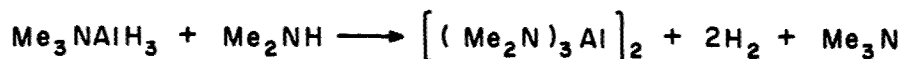
Attempted distillation of the resulting sesquiodide led to the recovery of dimethylaluminium iodide, bp 97° to $100^\circ/23$ mm, redistilled at 86° to $87^\circ/16$ mm, which gave the following analysis:

<u>CH_4</u>		<u>Al (as 8-hydroxyquinolate)</u>	
<u>Obs</u>	<u>Calc</u>	<u>Obs</u>	<u>Calc</u>
2.03	2.00	0.98	1.00

Methylaluminium diiodide was sublimed from the residue as a pale yellow solid, mp 65° to 71° , which agrees with the literature. These proposed reactions are being investigated.

a. Preparation of Bis(Dimethylamino) Aluminium Iodide

The preparation of the new compound bis(dimethylamino) aluminium iodide, $(\text{Me}_2\text{N})_2\text{AlI}$, was undertaken as a starting material for further studies on Al-N polymers. Aluminium iodide (Reference 9) was obtained as colourless crystals from aluminium wire and iodine vapour (1 mm) at 500° to 520° . Tris (dimethylamino) aluminium, $[(\text{Me}_2\text{N})_3\text{Al}]_2$, was made by the method of Ruff (Reference 10) with a modified procedure.



Solid methylammonium chloride was added to a suspension/solution of lithium aluminium hydride in dry ethyl ether and stirred at room temperature. The initially formed Me_3NAIH_3 was treated directly with gaseous dimethylamine. The solvent was removed and pale yellow $[(\text{Me}_2\text{N})_3\text{Al}]_2$ (mp 85° - 87° ; softening point 83°) sublimed under high vacuum; Ruff reported

mp 87° to 89°. $[(\text{Me}_2\text{N})_3\text{Al}]_2$ and $[\text{AlI}_3]_2$ in 2:1 mole proportions were fused together at 125° under nitrogen. Bis(dimethylamino) aluminium iodide sublimed under high vacuum at 135° (mp 120° -125°). The analysis is not yet completely satisfactory and recrystallisation from hexane/toluene as well as resublimation are being undertaken.

5. AMMONIA ADDUCTS OF PHENYLALUMINIUM COMPOUNDS

The formation of adducts of the type $\text{R}_3\text{Al} \cdot 2\text{NH}_3$ ($\text{R}_3\text{Al} = \text{Et}_3\text{Al}, \text{Et}_2\text{AlCl}$) was described earlier (Reference 11) and the corresponding adducts of triphenylaluminium and diphenylaluminium chloride have been briefly investigated. Tensiometric titrations at -46° have shown that triphenylaluminium forms 1:1 and 1:2 compounds with ammonia (see Figure 1), but the 1:2 adduct is dissociated at room temperature to ammonia and triphenylaluminium ammoniate. The latter is soluble in toluene and liquid ammonia, and its reaction with water is much less violent than that of triphenylaluminium. At -78°, an adduct, $\text{Ph}_3\text{Al} \cdot 6\text{NH}_3$, is detected but this has not been further studied.

Similar experiments with diphenylaluminium chloride suggested a 1:3 adduct at -46° and a 1:6 adduct at -78°. The form of the pressure-composition curves did not suggest the formation of ammonium chloride by ammonolysis (Reference 12). The 1:3 adduct lost approximately one mole of ammonia on warming to room temperature but the analysis (Found: C, 48.9; H, 6.6. $\text{Ph}_2\text{AlCl} \cdot 2\text{NH}_3$ requires C, 57.5, H, 6.4%) also suggests some elimination of benzene.

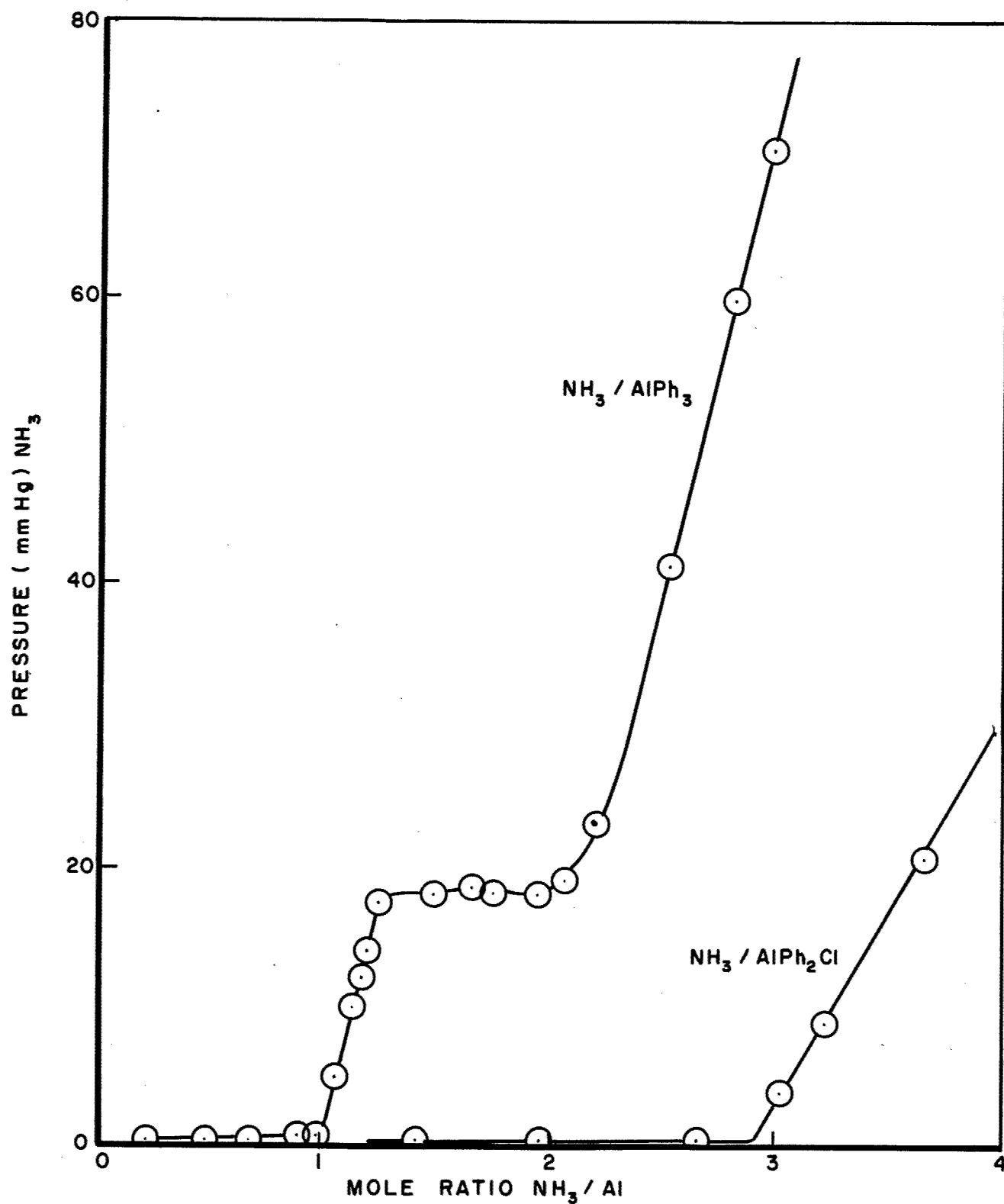


Figure 1. Pressure-Composition Study

SECTION II

ALUMINIUM PHOSPHORUS POLYMERS

1. INTRODUCTION

In an earlier report (Reference 4) we summarised the chemistry of aluminium-phosphorus compounds; these substances have recently been reviewed elsewhere (Reference 13). We have also described a method for the study of the simplest compounds containing Al-P bonds, i.e., donor-acceptor complexes, by NMR spectroscopy. Equilibrium constants derived from our previously reported plots of J_{P-C-H} versus Al/P mole ratio, using the method of Greenwood and Srivastava (Reference 14), are in Table IV.

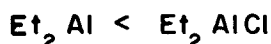
TABLE IV
EQUILIBRIUM CONSTANTS

Complex	$K = \frac{[R_3PAIR'_3]}{[R_3P][Al_2R'_6]^{1/2}}$
$Me_3P:BEt_3$	13
$Me_3P:AlEt_3$	60
$Me_2PhP:AlEt_3$	2.1
$MePh_2P:AlEt_3$	0.61
$Me_2PhP:AlEt_2Cl$	6.9

These equilibrium constants show a decrease in donor power of phosphorus in the series



and an increase in acceptor power of aluminium in the series



These values were derived for 2M solutions in benzene and it is easily shown that at this concentration the solvating characteristics of the solution change considerably in a series of samples with different Al/P mole ratios. It was felt that more meaningful relative equilibrium constants could be derived from more dilute solutions, and so a series of measurements at concentrations of 0.2M was begun. It became clear, however, that dilute solutions of triethylaluminium were difficult to handle quantitatively even in a dry box. Plots of coupling constant or chemical shift versus Al/P mole ratio were curved in such a way as to suggest that some hydrolysis or oxidation of triethylaluminium had occurred in the preparation of the samples for NMR measurements. More successful measurements were obtained for the $Me_3P/AlMe_3$ system; in these the trimethylphosphine, trimethylaluminium and solvent were

all transferred into well baked-out NMR tubes from a vacuum system fitted with mercury float valves. The results are shown in Table V.

TABLE V
NMR SPECTRA OF $\text{Me}_3\text{P}/\text{AlMe}_3$ MIXTURES (0.2M SOLUTION)

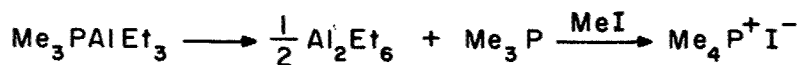
Tube	Al/P mole ratio	(P-Me)* cps	(Al-Me)* cps	$J_{\text{P-C-H}}$ cps
1	1.88	399.0	447.6	6.5
2	1.04	398.9	449.2	6.5
3	0.632	392.3	449.6	3.30
4	0.490	389.9	449.7	2.20
5	0.326	385.7	-	0
6	0	381.5	-	2.55

* Upfield from benzene

The experimental technique used here should be applicable to a wide range of donor-acceptor systems, and it should be possible to obtain useful equilibrium constant data.

2. REACTIONS OF DONOR-ACCEPTOR COMPLEXES

Complexes with Al-P bonds are completely decomposed by excess water and acid. This reaction, though violent, is useful for analysis and characterisation. A number of simpler reactions of donor-acceptor complexes have now been examined. Thus the adduct, $\text{Me}_3\text{PAlEt}_3$, reacted with one equivalent of methyl iodide at room temperature to give the quaternary salt, tetramethylphosphonium iodide, Me_4PI , and triethylaluminium. The adduct is known, from NMR measurements at 30° , to be slightly dissociated in dilute solution so that reaction with methyl iodide may proceed via dissociation and be aided by precipitation of the quaternary salt.

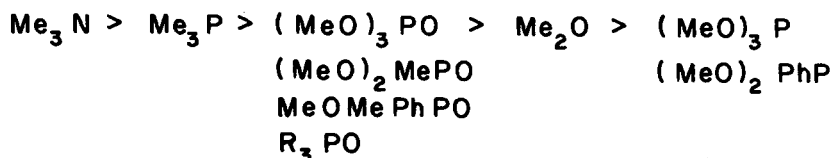


The possible intermediate, $[\text{Me}_4\text{P}][\text{Et}_3\text{AlI}]$, analogous to the known (Reference 15) compound, $[\text{Et}_4\text{N}][\text{Et}_3\text{AlI}]$, is thus unstable at room temperature.

The adduct, $\text{Me}_3\text{PAlEt}_3$, in methylcyclohexane, absorbed one equivalent of hydrogen chloride at -78° . The white product, presumably $[\text{Me}_3\text{PH}][\text{Et}_3\text{AlCl}]$, gave ethane as it warmed to room temperature and the complex, $\text{Me}_3\text{PAlEt}_2\text{Cl}$, was isolated quantitatively. This absorbed a further mole of hydrogen chloride at room temperature and at about 50° the product, $[\text{Me}_3\text{PH}][\text{Et}_2\text{AlCl}_2]$, gave ethane and the complex, $\text{Me}_3\text{PAlEtCl}_2$. In their reactions with

hydrogen chloride, the trimethylphosphine complexes are thus similar to the amine adducts of aluminium alkyls. Aluminium-carbon bonds are replaced before aluminium-phosphorus bonds.

Trimethylamine quantitatively displaced trimethylphosphine from its complex with triethylaluminium, in accord with earlier work (Reference 16) on trimethylaluminium adducts. In order to establish the relative basicities of phosphines and phosphorus esters towards triethylaluminium, a number of further displacement reactions were studied. Thus, the donors trimethylamine, trimethylphosphine, and dimethyl ether completely displaced trimethylphosphite from the adduct, $(\text{MeO})_3\text{PAlEt}_3$. Trimethylphosphite did not react with $\text{Me}_3\text{PAlEt}_3$, even though the displacement reaction should be aided by the relative volatility of the donors. Trimethylamine, trimethylphosphine, trimethylphosphate, dimethyl methylphosphonate and methyl methyl(phenyl)phosphinate all displaced dimethyl ether from its adduct with triethylaluminium. Dimethyl ether did not react with the trimethylphosphate and dimethyl methylphosphonate adducts with triethylaluminium, but quantitatively displaced triethyl- and trimethylphosphite as well as dimethyl phenylphosphonite. Trimethylphosphine displaced dimethyl methylphosphonate. It has been found by other workers (Reference 17) that phosphine oxides displace ethers from trialkylaluminium complexes. These results give the following order of decreasing base strength towards triethylaluminium as reference acid:



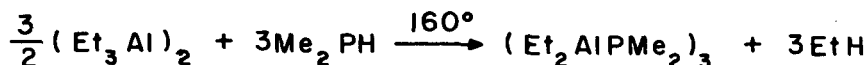
This order is similar to that found (Reference 18) for base strength towards trimethylborane, BMe_3 , (except that Me_3N , Me_3P are less sharply differentiated), but strikingly different from the order (Reference 19) towards boron hydride.



The driving force for the rearrangement of phosphite complexes of triethylaluminium, described in an earlier report (Reference 4), is thus related to the greater stability of the complexes of donors with phosphoryl groups.

3. PREPARATION AND REACTIONS OF DIETHYL(DIMETHYLPHOSPHINYL) ALUMINIUM

The compound diethyl(dimethylphosphinyl) aluminium, $\text{Et}_2\text{AlPMe}_2$, was chosen for the study of small ring compounds containing aluminium-phosphorus bonds, since it could easily be obtained from readily available starting materials by the reaction:



It was obtained from hexane solution as a white solid, mp 35° , and was trimeric in benzene. The PMR spectrum showed, in addition to peaks attributable to the aluminium-ethyl protons, a quartet centered at $\tau = 8.96$ due to the P-Me groups.

The NMR spectra of mixtures of $(\text{Et}_2\text{AlPMe}_2)_3$ and trimethylphosphine or $(\text{Et}_2\text{AlPMe}_2)_3$ and trimethylamine in benzene showed no reaction between the components at 30° . The failure of trimethylphosphine and trimethylamine to cleave the Al-P ring in the trimer was confirmed

by pressure-composition studies at 20° and at -46°, and is in accord with earlier data (Reference 16) on $(\text{Me}_2\text{AlPHe}_2)_3$. Dimethylphosphine, similarly, did not react with $(\text{Et}_2\text{AlPMe}_2)_3$. Dimethylamine, however, readily displaced dimethylphosphine, and proceeded quantitatively according to the reaction:



This illustrates the strong base strength of the amine and the marked stability of small Al-N compared with Al-P rings.

4. PREPARATION OF THE COMPOUNDS $(\text{RPAIP})_x$

The ready isolation of the crystalline tetramer (Reference 3), $(\text{PhAlNPh})_4$, suggested that an attempt to make the phosphorus analogue might be worthwhile. The complex, $\text{Ph}_3\text{AlPhH}_2$, obtained by mixing equimolar amounts of phenylphosphine and triphenylaluminum, readily dissociated at room temperature, reflecting the weak basic character of the phosphine, but benzene was eliminated on heating (Tables VI and VII).

TABLE VI
ELIMINATION OF HYDROCARBONS FROM PHENYLPHOSPHINE
ADDUCTS OF ORGANOALUMINIUM COMPOUNDS

R_3Al (mmole)	PhPH_2 (mmole)	Solvent	Conditions	Products
EtAlCl_2 (10.3)	10.9	toluene (25 ml)	20°	PhPH_2 , EtAlCl_2 recovered
EtAlCl_2 (17.7)	17.1	none	100° (24 hr) 120° (3 hr)	EtH (33.7 mmole, 99%) amorphous ClAlPPh
Et_3Al (33.2)	34.1	Tetralin (25 ml)	200° (6 hr)	EtH (62.7 mmole, 94.3%) amorphous EtAlPPh^*
Ph_3Al (3.99)	4.24	toluene (25 ml)	20°	PhPH_2 , AlPh_3 recovered
Ph_3Al (4.00)	4.01	none	170° (4 hr)	PhH (7.75 mmole) amorphous PhAlPPh^{**}
Ph_3Al (15.6)	15.5	xylene (20 ml)	145° (9 hr)	PhH (26.3 mmole, 85%) soluble PhAlPPh
Ph_3Al (20.0)	21.2	Tetralin (20 ml)	200° (10 hr)	PhH (37.8 mmole) insoluble PhAlPPh
Ph_3Al (4.18)	4.67	Tetralin (27 ml)	200° (17 hr)	PhH (9.05 mmole) soluble PhAlPPh

* dec ~ 260°; ** charred 230°, did not sublime below 370°

TABLE VII

ANALYSES

Compound	Found	Calculated
ClAlPPh	Al, 15.7; Cl, 20.9	Al, 15.8; Cl, 20.9%
EtAlPPh	Al, 14.3; Et, 16.8	Al, 16.4; Et, 17.7%
PhAlPPh	Al, 11.3; C, 68.9; H, 5.6%	Al, 12.7; C, 67.9; H, 4.7

Reactions in the absence of solvents confirmed the stoichiometry (two moles of benzene per aluminium were obtained at 200°) but the product was an involatile, amorphous solid which was not soluble in common organic solvents. The product obtained in refluxing Tetralin, provided the solution was not too concentrated, was freely soluble in aromatic hydrocarbons but was precipitated by paraffinic solvents. Molecular weight measurements in benzene indicated tetrameric species, but attempts to crystallise the solid have been unsuccessful. All the samples obtained appeared amorphous in polarised light and failed to give X-ray powder patterns. The solid was involatile in vacuum and could not be sublimed below 350°; this involatility prevented measurement of its mass spectrum.

Similar results were obtained from experiments on the adducts of phenylphosphine with triethylaluminium and diethylaluminium chloride. In both cases, two moles of ethane per aluminium were readily eliminated but the products were amorphous and insoluble. The colours deepened on heating to ca 250°, perhaps indicating defect structures, and the materials decomposed (300°-400°) before sublimation (10-3 mm). This is in accord with observations by Coates (Reference 20), but there is still no explanation for the facts that soluble low polymeric materials cannot be obtained in crystalline form. No attempts have been made to isolate the intermediates, R_2AlPPh .

The chemistry in the formation of Al-P frameworks is thus similar to that involved in the formation of the analogous Al-N compounds, but the products seem to be even more difficult to isolate. The greater stability of the Al-N compounds, $R_2AlNR'_2$, with respect to attack by bases has been shown by displacement reactions (Section II, Par. 3), but experiments on the compounds, $RAIPR'$, have not yet been made.

Organoaluminium compounds absorb ammonia to form a series of adducts with several moles of ammonia per aluminium (Reference 11). In order to see whether a similar series of adducts with phosphine could be isolated, the interaction of ethylaluminium dichloride and phosphine was studied. However, no phosphine was absorbed by a solution of ethylaluminium dichloride in toluene at -78° and there was no reaction while ethylaluminium dichloride was heated in phosphine at 50°. (The reaction between phosphine and aluminium trichloride is reported (Reference 20) to occur only on heating). It seems, therefore, that phosphine is too weak a base to form adducts with organoaluminium compounds.

5. NMR DATA ON ADDUCTS OF PHOSPHORUS ESTERS WITH ORGANOALUMINIUM COMPOUNDS

A number of NMR measurements were made during this investigation and some of the chemical shifts and coupling constants are tabulated in Tables VIII and IX. This data is being

TABLE VIII

NMR DATA

Compound	Solvent and Concentration	POCH ₃	PCH ₃	^J P-O-C-H (cps)	^J P-C-H (cps)	AlCH ₂	AlCH ₂ CH ₃	Δ(Al) (ppm)
(MeO) ₃ P	2M benzene	6.67	-	10.7	-	-	-	-
(MeO) ₃ P: 0.38 AlEt ₃	2M benzene	6.70	-	10.4	-	9.84	8.70	1.14
(MeO) ₃ PAEt ₃	2M benzene	6.70	-	10.2	-	9.90	8.75	1.15
(MeO) ₃ PAEt ₃	none	7.37		9.6		11.14	10.0	1.14
(MeO) ₂ MePO								
(MeO) ₂ MePO:0.38 AlEt ₃	2M benzene	6.68	8.96	11.5	17.6	9.91	8.64	1.27
(MeO) ₂ MePO:AlEt ₃	2M benzene	6.70	8.93	11.4	17.0	10.0	8.71	1.29
(MeO) ₂ MePO:1.9 AlEt ₃	2M benzene	6.65	8.95	10.2	18.0	10.0	8.9	1.14
(MeO) ₂ MePOAlEt ₃	none	7.16	9.69	11.4	18.0	11.33	10.0	1.33
(MeO) ₂ PhPAEt ₃	none	7.39	-	10.2	-	11.1	10.0	1.10
(MeO)MePhPOAlEt ₃	none	7.49	9.29	12.0	15.0	11.29	10.0	1.29
(MeO) ₃ POAlEt ₃	none	-	-	12.0	-	-	-	-
(MeO) ₃ POAlEtCl ₂	none	6.30	-	11.8	-	9.85	8.82	1.03
Me ₃ POAlEt ₃	2% benzene	(Ref. 17)						1.18
Et ₃ POAlEt ₃	2% benzene		.					1.18

TABLE IX
NMR DATA

Compound	Solvent and Concentration	POCH_2	POCH_2CH_3	$\Delta(\text{P})$ (ppm)	$\text{J}_{\text{P-O-C-H}}$ (cps)	AlCH_2	AlCH_3	$\Delta(\text{Al})$ (ppm)
$(\text{EtO})_3\text{P}$	none	6.18	8.81	2.63	7.2	-	-	-
$(\text{EtO})_3\text{P:1/2AlEt}_3$	M benzene	6.24	8.91	2.67	7.1	9.72	8.59	1.13
$(\text{EtO})_3\text{PAEt}_3$	M benzene	6.23	8.95	2.72	7.1	9.75	8.60	1.15
$(\text{EtO})_3\text{PAEt}_3$	none	7.00	9.72	2.72	7.2	11.07	10.0	1.07
$(\text{EtO})_3\text{PAEt}_2\text{Cl}$	M benzene	6.22	8.88	2.66	7.2	9.77	8.63	1.14
$(\text{EtO})_3\text{PAEtCl}_2$	M benzene		8.91					
$(\text{EtO})_3\text{PAEtCl}_2$	none	5.53	8.57	3.04	6.9	9.89	8.95	0.94
$(\text{EtO})_2\text{EtPO}$	none	5.93	8.73	2.80	7.5	-	-	-
$(\text{EtO})_2\text{EtPOAlEtCl}_2$	none	6.71	9.63	2.92	7.3	10.0	11.02	1.02
$(\text{EtO})_3\text{PO}$	none	5.93	8.72	2.79	7.5			
$(\text{EtO})_3\text{POAlEtCl}_2$	none	5.64	8.63	2.99	7.5	10.04	8.99	1.05

examined to see whether any generalisations may be made which are useful diagnostically in compounds of unknown structure. Several preliminary conclusions may be shown.

a. The chemical shifts of donor-acceptor complexes are very sensitive to concentration changes. This is to be expected since in passing from pure complex to dilute solution there are large changes in bulk susceptibility. Comparisons between complexes are thus valid only for measurements in dilute solution.

b. In general, resonances are at lower fields in benzene solution than for neat complexes.

c. The largest changes in chemical shift on complex formation are observed for the Al-CH_2 protons. These are the nearest to the electronic changes at the aluminium atom. In general, the "internal chemical shift", Δ , between the Al-CH_2 and $\text{Al-CH}_2\text{-CH}_3$ protons seems to be almost independent of concentration. This is in contrast (Reference 22) to the situation for the free (dimeric) acceptors for which a marked dependence of Δ on solvent was observed. For triethylaluminium complexes with Al-P bonds, a Δ value of 1.13 to 1.15 ppm is obtained, and for complexes with Al-O-P bonds a value of about 1.27 to 1.33 ppm. Under similar conditions, e.g., molar solutions in benzene, resonances for oxygen complexes appeared at higher field than those where phosphorus was the donor atom.

d. The internal chemical shift for ethylaluminium dichloride ($\sim 1.02\text{-}1.05$ ppm) is less than for triethylaluminium complexes. For the pure liquid acceptors an increase in Δ from triethylaluminium to diethylaluminium chloride has been reported (Reference 22).

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